

## PYROXENE CRYSTAL CHEMISTRY AND THE EVOLUTION OF ECLOGITES IN THE MANTLE.

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Mantle eclogites as represented in inclusions in South African kimberlites show a wide variation in major element composition from coesite- or corundum-bearing grosspydites to kyanite eclogites to Fe- and Mg-rich biminerallitic eclogites. In major element composition, the biminerallitic samples resemble MORB; the coesite grosspydites resemble anorthosite; and the corundum grosspydites do not resemble any crustal rock type. In rare earth elements, the biminerallitic samples also resemble MORB, having concentrations of 2 to 20 times chondritic values with flat to slightly LREE-depleted patterns. The grosspydites (both coesite and corundum-bearing) show characteristic depletions in both light and heavy REE and slight enrichments in the middle REE with maxima at Eu (Caporuscio and Smyth, 1990). Oxygen isotope values range from about +2 to +10‰, a much greater range than exhibited by other mantle samples, but do not appear to vary systematically with major-element compositions.

In many samples, particularly the grosspydites, there is abundant evidence of garnet and garnet-plus-kyanite exsolution from the clinopyroxene. We have also observed epitaxial rutile and phlogopite that have apparently exsolved from clinopyroxene. Re-assembling the clinopyroxene from exsolved phases we see an unexpectedly complex crystal chemistry. Textures in two corundum grosspydites suggest that most of the garnet and clinopyroxene in the rock had exsolved from a single precursor pyroxene that could not have existed at pressures less than about 3 GPa. These observations strongly support the hypothesis of Lappin (1978) that the grosspydites may be the result of an accumulation of hyperaluminous pyroxene at pressures greater than 3 GPa (Smyth et al., 1984, 1989).

Alternatively, other recent studies have favored an origin for the grosspydites as subducted feldspathic cumulates (MacGregor and Manton, 1986; Shervais et al., 1988, Taylor and Neal, 1989, Neal et al., 1990). This hypothesis accounts for the large variation in oxygen isotopic values in these rocks, although not in any consistent or systematic way. However, it fails to account for corundum-normative grosspydites; and it fails to account for the extreme values of radiogenic isotope ratios observed in these rocks (Shervais et al., 1988; Caporuscio, 1988; Neal et al., 1990).

The key to understanding these rocks, however, appears to lie in understanding the crystal chemistry of the pyroxenes. Smyth (1980) reported microprobe data indicating up to 9 mole percent vacancy in the M cation sites. McCormick (1986) located the cation vacancy in the M2 site by means of electron channeling and X-ray single crystal diffraction. The reconstructed exsolved pyroxene reported by Smyth et al. (1984) would have had about 17% M2 vacancy. Smyth et al. (1991) report IR spectra indicating up to 1800 ppm by weight OH in one

sample and a linear correlation of cation deficiency (vacancy) with H content. Extrapolating this relationship, we would infer that the most vacancy-rich pyroxene analyzed would have about 2600 ppm by weight OH and the reconstructed precursor pyroxene about 0.5 wt% OH. We are currently pursuing X-ray and neutron single crystal diffraction studies of this pyroxene to structurally locate the hydrogen.

This is much more H than any other nominally anhydrous phase common in the eclogite or peridotite suite of rocks, with the possible exception of rutile (Rossman and Smyth, 1990). It is two to three orders of magnitude more than co-existing garnet. In the eclogite-rich mantle suggested by Anderson (1984), clinopyroxene could be the dominant hydrous phase. Further, the H released from the pyroxene on cooling from solidus temperatures provides a source of H for auto-metasomatism of the eclogites. This would account for at least part of the ubiquitous secondary assemblage observed on nearly every grain boundary in the eclogites.

The REE composition of the grosspyrites is also consistent with an origin by high pressure igneous accumulation of clinopyroxene. In particular, the MREE enrichments and much lower total REE contents of the grosspyrites are typical of clinopyroxene-liquid fractionations, and inconsistent with plagioclase-liquid fractionations.

The great range of oxygen isotope values observed for these rocks suggests a low-temperature process. However, we have observed mineral-mineral fractionations up to 3.0‰ for a garnet-coesite pair indicating that significant fractionation can indeed occur at mantle temperatures. Further, we observe a correlation of garnet-clinopyroxene fractionation of oxygen isotopes with vacancy (and presumably OH) content. This suggests that oxygen isotopes might be disturbed or affected by the H-content or evolution of hydrous fluid from the pyroxene. However, these observations do not preclude the involvement of a low temperature process in that the silicate liquids may be the result of partial melting of subducted material.

In summary, it appears that clinopyroxene crystal chemistry may control much of the chemical evolution of eclogites in the mantle. The major and trace element whole-rock compositions seem to be the result of igneous accumulation of a liquidus pyroxene at pressures above 3 GPa, and exsolution textures seem to require that some of these rocks were almost single-phase pyroxenes. Hydrogen contents of eclogitic clinopyroxene are the largest of any pyroxene and correlate with M2 cation vacancies. The large amounts of structurally-bound OH may allow clinopyroxene to be the dominant hydrous phase in some possible mantle compositions. Further, evolution of H and other incompatible elements from clinopyroxene may account for some of the ubiquitous secondary phases observed on grain boundaries in mantle eclogites.

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